1.0	4.5	2.8	2.5
5.0	3.2	2.2
5.6	3.6
1.1	4.0	2.0
1.8
1.25	1.4	1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

OFFICE OF NAVAL RESEARCH

Contract N00014-84-G-0201

Task No. 0051-865

Technical Report #10

Electrochemistry and Spectro-Electrochemistry of Mononuclear and
Binuclear Cobalt Phthalocyanines

By

W.A. Nevin, M.R. Hempstead, W. Liu, C.C. Leznoff, and A.B.P. Lever

in the

Inorganic Chemistry

York University
Department of Chemistry, 4700 Keele St., North York
Ontario, Canada   M3J 1P3

86 11 19 039

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY Unclassified	3. DISTRIBUTION / AVAILABILITY OF REPORT As it appears on the report
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report #	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201

| 8c. ADDRESS (City, State, and ZIP Code) | 10. SOURCE OF FUNDING NUMBERS |

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
Electrochemistry and Spectro-Electrochemistry of Mononuclear and Binuclear Cobalt Phthalocyanines

12 PERSONAL AUTHOR(S) Nevin, William Andrew; Hempstead, Michael R.; Liu, Wei; Leznoff, Cliff C.; Lever, Alfred Beverley Philip

13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM Oct.84 TO _____	14. DATE OF REPORT (Year, Month, Day) September, 1986	15. PAGE COUNT

16 SUPPLEMENTARY NOTATION

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Spectroelectrochemistry, Binuclear Phthalocyanines, Phthalocyanine Electrochemistry

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The electrochemistry of [,9,16,23-tetra(neopentoxy)phthalocyanato]cobalt, and some binuclear analogs, has been studied in dichlorobenzene and in dimethylformamide. The redox mechanisms and species on the electrode are discussed. Using an optically thin electrode, the electronic spectra of seven different oxidation states of the mononuclear derivative are reported. Data for a selection of oxidation states of several binuclear species are also presented.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Harold E. Guard	22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL

DD FORM 1473, 34 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

TECHNICAL REPORT DISTRIBUTION LIST, 051A

Dr. M. A. El-Sayed
Department of Chemistry
University of California
Los Angeles, California 90024

Dr. E. R. Bernstein
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80521

Dr. J. R. MacDonald
Chemistry Division
Naval Research Laboratory
Code 6110
Washington, D.C. 20375-5000

Dr. G. B. Schuster
Chemistry Department
University of Illinois
Urbana, Illinois 61801

Dr. J.B. Halpern
Department of Chemistry
Howard University
Washington, D.C. 20059

Dr. M. S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. A. Paul Schaap
Department of Chemistry
Wayne State University
Detroit, Michigan 49207

Dr. W.E. Moerner
I.B.M. Corporation
Almaden Research Center
650 Harry Rd.
San Jose, California 95120-6099

Dr. A.B.P. Lever
Department of Chemistry
York University
Downsview, Ontario
CANADA M3J1P3

Dr. John Cooper
Code 6173
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. George E. Walrafen
Department of Chemistry
Howard University
Washington, D.C. 20059

Dr. Joe Brandelik
AFWAL/AADO-1
Wright Patterson AFB
Fairborn, Ohio 45433

Dr. Carmen Ortiz
Consejo Superior de
   Investigaciones Científicas
Serrano 121
Madrid 6, SPAIN

Dr. John J. Wright
Physics Department
University of New Hampshire
Durham, New Hampshire 03824

Dr. Kent R. Wilson
Chemistry Department
University of California
La Jolla, California 92093

Dr. G. A. Crosby
Chemistry Department
Washington State University
Pullman, Washington 99164

Dr. Theodore Pavlopoulos
NOSC
Code 521
San Diego, California 91232

OL/1113/86/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003

Dr. J. Driscoll
Lockheed Palo Alto Research
  Laboratory
3251 Hanover Street
Palo Alto, California 94304

Dr. D. N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, Utah 84602

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. Roger Belt
Litton Industries Inc.
Airtron Division
Morris Plains, NJ 07950

Dr. Ulrich Stimming
Department of Chemical Engineering
Columbia University
New York, NY 10027

Dr. Manfred Breiter
Institut fur Technische Flektrochemie
Technischen Universitat Wien
9 Getreidemarkt, 1160 Wien
AUSTRIA

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. C. E. Mueller
The Electrochemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Dr. Sam Perone
Chemistry & Materials
  Science Department
Lawrence Livermore National Laboratory
Livermore, California 94550

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. A. B. Ellis
Chemistry Department
University of Wisconsin
Madison, Wisconsin 53706

Dr. Steven Greenbaum
Department of Physics and Astronomy
Hunter College
695 Park Ave.
New York, NY 10021

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. M. Wrighton
Chemistry Department
Massachusetts Institute
  of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Donald E. Mains
Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, Indiana 47522

S. Ruby
DOE (STOR)
Room 5E036 Forrestal Bldg., CE-14
Washington, D.C. 20595

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Donald W. Ernst
Naval Surface Weapons Center
Code R-33
White Oak Laboratory
Silver Spring, Maryland 20910

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. Aaron Fletcher
Naval Weapons Center
Code 3852
China Lake, California 93555

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Laboratories, Inc.
Norwood, Massachusetts 02062

Dr. Aaron Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH UNITED KINGDOM

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. John Wilkes
Air Force Office of Scientific
  Research
Bolling AFB
Washington, D.C. 20332

Dr. D. Rolison
Naval Research Laboratory
Code 6171
Washington, D.C. 20375-5000

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. B. P. Lever
Chemistry Department
York University
Downsview, Ontario M3J1P3

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 633, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
 and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

M. L. Robertson
Manager, Electrochemical
 and Power Sources Division
Naval Weapons Support Center
Crane, Indiana 47522

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Nathan Lewis
Department of Chemistry
Stanford University
Stanford, California 94305

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH UNITED KINGDOM

Dr. E. Anderson
NAVSEA-56Z33 NC #4
541 Jefferson Davis Highway
Arlington, VA

Dr. Bruce Dunn
Department of Engineering &
 Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. Richard Pollard
Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Dr. M. Philpott
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Donald Sandstrom
Boeing Aerospace Co.
P.O. Box 3999
Seattle, Washington 98124

Dr. Carl Kannewurf
Department of Electrical Engineering
 and Computer Science
Northwestern University
Evanston, Illinois 60201

Dr. Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Robert Somoano
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Judith H. Ambrus
NASA Headquarters
M.S. RTS-6
Washington, D.C. 20546

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. H. Tachikawa
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Dr. Farrell Lytle
Boeing Engineering and
  Construction Engineers
P.O. Box 3707
Seattle, Washington 98124

Dr. Robert Gotscholl
U.S. Department of Energy
MS G-226
Washington, D.C. 20545

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402

Dr. Martha Greenblatt
Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

Dr. John Wasson
Syntheco, Inc.
Rte 6 - Industrial Pike Road
Gastonia, North Carolina 28052

Dr. Walter Roth
Department of Physics
State University of New York
Albany, New York 12222

Dr. Anthony Sammells
Eltron Research Inc.
4260 Westbrook Drive, Suite 111
Aurora, Illinois 60505

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymer Science and Standards
  Division
National Bureau of Standards
Washington, D.C. 20234

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. John Owen
Department of Chemistry and
  Applied Chemistry
University of Salford
Salford M5 4WT ENGLAND

Dr. Boone Owens
Department of Chemical Engineering
  and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Menahem Anderman
W.R. Grace & Co.
Columbia, MD 20144

Dr. J. O. Thomas
University of Uppsala
Institute of Chemistry
Box 531
S-751 21 Uppsala, Sweden

Dr. O. Stafsudd
Department of Electrical Engineering
University of California
Los Angeles, California 90024

ELECTROCHEMISTRY AND SPECTRO-ELECTROCHEMISTRY OF MONONUCLEAR AND BINUCLEAR COBALT PHTHALOCYANINES.

W.A. Nevin, M.R. Hempstead, W.Liu[1], C.C. Leznoff, and A.B.P. Lever[*]

Dept. of Chemistry, York University, North York, Ontario, Canada M3J 1P3

Abstract

The electrochemistry of [2,9,16,23-tetra(neopentoxy)phthal-ocyanato]cobalt, and some binuclear analogs, has been studied in dichlorobenzene and in dimethylformamide. The redox mechanisms and species on the electrode are discussed. Using an optically thin electrode, the electronic spectra of seven different oxidation states of the mononuclear derivative are reported. Data for a selection of oxidation states of several binuclear species are also presented.

Introduction

The electrochemistry and spectro-electrochemistry of metallo-porphyrins have been extensively studied.[2-16] However, relatively little spectro-electrochemistry has been carried out on phthal-ocyanines[17-25] due to their low solubilities in suitable solvents for electrochemistry which limits the use of optically transparent thin layer electrodes (OTTLE). Such studies are desirable in view of the

potential use of phthalocyanines as electrocatalysts[26-28], where an understanding of the nature of the redox processes of the phthalocyanine molecule is essential for the design of more efficient catalysts. The redox processes may occur at either the central metal atom or the phthalocyanine ring, but this cannot usually be distinguished using electrochemistry alone. Spectro-electrochemical studies of the phthalocyanines are also important with regard to their possible use as electrochromic materials.[24,29,30]

Recently[31-33], we have reported the synthesis of a series of binuclear phthalocyanines formed by linking units of tri(neopentoxy) phthalocyanine (TrNPc) together through a benzene ring by bridges of 1,2,4 or 5 atoms. The three neopentoxy groups are randomly distributed in the 4 or 5 positions of the unlinked benzene rings and provide high solubility for the phthalocyanines in a wide range of organic solvents, such as toluene, o-dichlorobenzene (DCB), dichloromethane (DCM) and N,N- dimethylformamide (DMF). These complexes, and in particular the cobalt derivatives, have been the subject of recent investigations as oxygen reduction catalysts and as multi-electron redox catalysts.[26, 34] We report here an electrochemical and spectro-electrochemical study on the cobalt derivatives of mononuclear and binuclear neopentoxy phthalocyanines in DCB and DMF.

The purpose of this work was to obtain, for the first time, the electronic spectra of a wide range of electrochemically generated CoPc redox species in organic solution, and, in addition, to determine any possible effects of coupling in the binuclear species on the redox processes and spectra. Several scattered reports of CoPc redox species exist in the literature; however these are incomplete and are often reported in the solid state where Davydov effects will distort the

spectra.

Spectra are presented here for a series of seven electro-chemically generated redox species of the mononuclear derivative.

Of relevence to this presentation are the following species, with their abbreviations (Figure 1) (the number in parenthesis is the number of bridging atoms connecting the two phthalocyanine rings):

label

CoTNPc   [3,9,16,23-tetra(neopentoxy)phthalocyanato]cobalt. This is the mononuclear control molecule.

EtMeO(5)[CoTrNPc]$_2$ phthalocyanine rings linked via -OCH$_2$C(Me)(Et)CH$_2$O-.

Cat(4)[CoTrNPc]$_2$ phthalocyanine rings linked via -O-C$_6$H$_4$-O- (o-catechol).

C(2)[CoTrNPc]$_2$ phthalocyanine rings linked via -CH$_2$CH$_2$-.

O(1)[CoTrNPc]$_2$ phthalocyanine rings linked via a single oxygen (ether) bridge.

These binuclear complexes can exist in various conformations depending upon the nature of the bridging unit.[35] The EtMeO(5) and Cat(4) species can close in a "clamshell" - like fashion (see Figure 1), while geometrical constraints of the bridge restrict the C(2) and O(1) species to an open conformation. Electronic coupling between the

phthalocyanine rings may occur through space or through the bridge.[35] For the series of binuclear cobalt derivatives, the degree of electronic interaction between the phthalocyanine rings has been found to increase in the order[34]:

$$C(2) < EtMeO(5) < Cat(4) < O(1)$$

The nomenclature CoTNPc or $[CoTrNPc]_2$ is used for a general species of undefined oxidation state, while for specific compounds, the oxidation states of both metal and phthalocyanine are defined. The Pc(-2) state is the standard oxidation state for the phthalocyanine ring.[36,37]

Experimental

The species H_2TNPc[31], CoTNPc[31], $EtMeO(5)[CoTrNPc]_2$[31], $Cat(4)[CoTrNPc]_2$[32], $C(2)[CoTrNPc]_2$[32] and $O(1)[CoTrNPc]_2$[33] were prepared by the literature routes cited. N,N-dimethylformamide (DMF) (Aldrich, Gold Label, anhydrous, H_2O < 0.005%, packaged under nitrogen) o-dichlorobenzene (DCB) (Aldrich, Gold Label), dichloromethane (DCM) (Aldrich, Gold Label) and acetonitrile (Aldrich, Gold Label) were used as supplied. Tetrabutylammonium perchlorate (TBAP) (Kodak) was recrystallised from absolute ethanol and dried at 50° C under vacuum for two days. $[Co(III)(CN)_2TNPc(-2)]K$[38-40] was prepared by adding a 10-fold excess of KCN to a solution of $Co(II)TNPc(-2)$ in DCM/CH_3CN (2:1).

Electronic spectra were recorded with a Hitachi-Perkin Elmer Microprocessor model 340 spectrometer or a Guided Wave Inc. model 100-20 Optical Waveguide Spectrum Analyser with a WW100 fibre optic

probe. Electrochemical data were obtained using a Pine model RDE 3 double potentiostat, or with a Princeton Applied Research (PARC) model 173 potentiostat, or with a PARC model 174A Polarographic Analyser coupled to a PARC model 175 Universal Programmer. Cyclic voltammetry and differential pulse polarography were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Drilab using a conventional three-electrode cell. A platinum disc described by the cross-sectional area of a 27 gauge wire (area ca. 10^{-3} cm^2), sealed in glass, was used as the working electrode in DCB solution, and a platinum wire in DMF solution. A platinum wire served as the counter electrode, and a silver wire was used as a quasi-reference electrode. Potentials were referenced internally to the ferrocenium/ ferrocene (Fc$^+$/Fc) couple (+0.16V vs SCE).[41] All DMF solutions were prepared within the dry-box. The DCB solutions were prepared in air, degassed by repeated freeze-pump-thaw cycles, and then transferred to the dry-box.

Spectro-electrochemical measurements were made with an optically transparent thin layer electrode cell utilising a gold minigrid (500 lines/in)[42], in conjunction with the Hitachi-Perkin Elmer spectrometer; or by using a bulk electrolysis cell, consisting of a platinum plate working electrode, platinum flag counter and silver wire quasi-reference electrode (reference and counter electrodes were separated from the working compartment by medium glass frits). Spectra were recorded during bulk electrolysis by immersing the Guided Wave fibre optic probe in the solution, degassed with argon.

Solutions for electrochemistry and spectro-electrochemistry contained 0.1-0.3M TBAP, as supporting electrolyte.

Results   and   Discussion

Electrochemistry   in   DCB   Solution

Figure 2(a) shows a typical cyclic voltammogram of CoTNPc in DCB. The molecule undergoes two quasi-reversible one-electron reductions and three quasi-reversible one-electron oxidations within the limit of the solvent ($i_a = i_c$, $i \propto \sqrt{v}$). Half-wave potentials and peak separations at a scan rate (v) of 20 mV/s are given in Table I.

The binuclear [CoTrNPc]$_2$ complexes show very similar voltammetry to the mononuclear species, although the waves are generally broader and weaker. However, well defined peaks were obtained by differential pulse polarography; Figure 3 compares the results for O(1)[CoTrNPc]$_2$ with those of CoTNPc in DCB. Values of half-wave potentials measured for the binuclear complexes in DCB are given in Table I. Note that the potential of the second oxidation couple (II) is very sensitive to traces of anions which can coordinate to the cobalt atom.

No splitting of the redox peaks was seen for any of the binuclear complexes, such as has been observed for the Co(II)/Co(I) couple of a "clamshell" cobalt porphyrin[13] and the Co(II)/Co(I) and Co(III)/Co(II) couples of "face-to-face" cobalt porphyrins.[13,14] This splitting is attributed to interactions between the two cobalt atoms which are held in close proximity by the ligand geometry, resulting in overlap of their d_z2 orbitals along the cobalt-cobalt axis. The size of the splitting is proportional to the magnitude of the interaction between the cobalt atoms. In the case of the binuclear phthalocyanines studied here,

however, the two CoTrNPc units of each molecule oxidise or reduce "simultaneously", even for those species known to exist in a closed "clamshell" conformation in solution. Either electronic coupling between the cobalt atoms is not sufficient to cause an observable splitting of the couples, or more likely, in a preliminary chemical step, the more coupled conformations rearrange to a less coupled conformation, prior to the electron transfer. The electronic coupling IS sufficient to be observed as a perturbation of the electronic spectra of these cobalt species.[34]

Note that for the "clamshell" porphyrin[13], linkage occurs via bridges between two benzene rings of each porphyrin ring thus giving a more rigid geometry than for the binuclear phthalocyanines reported here. The broadening of the redox waves of the binuclear compounds relative to CoTNPc may arise because of the mixture of isomers which is present, having slightly different redox potentials.

For comparison, half-wave potentials for the metal-free mononuclear complex, H_2TNPc, in DCB solution are also given in Table I. Two quasi-reversible one-electron reductions and two quasi-reversible one-electron oxidations are observed, corresponding to the first and second reductions and oxidations, respectively, of the phthalocyanine ring.

Spectro-electrochemistry in DCB Solution

Typical absorption spectra for Co(II)THPc(-2), and the "closed" and "open" binuclear species, $EtMeO(5)[Co(II)TrNPc(-2)]_2$ and $C(2)[Co(II)TrNPc(-2)]_2$, respectively, are shown in Figure 4. The binuclear species show an additional band centred at ca. 50 nm to the

blue of the normal Q band as a result of interaction between the phthalocyanine rings through "exciton coupling."[34,35] Spectroscopic data for CoTNPc species are given in Table II.

Polarisation of a solution of CoTNPc in DCB in the OTTLE at 200 mV negative of the first reduction couple (IV), results in the spectroscopic changes shown in Figure 5, and a change of colour from blue to yellow. Isosbestic points are observed at 325, 360, 395, 557 and 692 nm. The spectrum is typical of a Co(I)Pc(-2) species[17,19,20,39,40,43,44], characterised by the appearance of a strong band at 475 nm, assigned as a metal-to-ligand charge transfer from Co(I)Pc(-2)[d(xz,yz)]---> $\pi^*(1b_{1u})$Pc(-2)[40,45,46], and a red shift and decrease in intensity of the Q band. The reduced species is fully reversible to the starting material by oxidation positive of the first reduction couple.

Polarisation at 200 mV negative of the second reduction couple (V) results in a change from yellow to a pink solution, the spectrum of which is shown in Figure 6. The observed small red shift of the MLCT band and decrease in intensity of the Q band relative to the first oxidation product are similar to those obtained by Clack and Yandle[20] for the chemical formation of the species $[Co(I)Pc(-3)]^{2-}$ in DMF, and by Le Moigne and Even[43] for a chemically reduced thin film of CoPc. In addition, a weak near ir band occurs at 950 nm. The appearance of a band in the region of 950 nm appears characteristic of the ligand-reduced species, as has been observed previously for a number of metallophthalocyanines.[20,46] Re-oxidation at a potential positive of couple (IV) generates the starting material with ca. 20% decrease in the Q band intensity (no decomposition products absorbing in the region of 300-1600 nm were observed).

Oxidation of CoTNPc in DCB in the OTTLE at 200 mV positive of the first oxidation couple (III), results in a rapid decrease in the intensity of the Q band and the formation of a pale pink solution. The broad, low-intensity spectrum, shown in Figure 7, is unlike those observed for Co(III) phthalocyanine species[34,39,40,47,48], but is very similar in appearance to those reported for the ligand oxidations of phthalocyanines[21,22,49] to form the Pc cation radical species, $[Pc(-1)]^+$. Since this redox couple is a one-electron process, it must correspond to the one-electron oxidation of the phthalocyanine ring, to give the species $[Co(II)TNPc(-1)]^+$. Similarly, a broadening and lowering of intensity of the bands in the visible region is typically observed for the ligand oxidation in metalloporphyrins.[2,50-52] The results are in agreement with those of Gavrilov et al.[24], who reported the oxidation of Co tetra-4-t-butyl- phthalocyanine in DCB. In contrast, the first oxidation of cobalt tetraphenylporphyrin (CoTPP) in non-coordinating solvents has been shown to occur on the cobalt atom.[3-5]

Polarisation of the OTTLE at 200 mV positive of the second oxidation couple (II) results in the formation of a red-brown solution, with a spectrum shown in Figure 7. The broad, three-banded spectrum is typical of those found previously for chemically oxidised CoPc in $CHCl_3$[47] and as a thin film[37], and assigned to a $[Co(III)Pc(-1)]^{2+}$ species. Thus, the second oxidation occurs on the metal to give $[Co(III)TNPc(-1)]^{2+}$.

Polarisation of the OTTLE positive of the third oxidation couple (I) gives a decrease in absorption intensity to a broad spectrum with bands centred at 430 and 630 nm, as shown in Figure 7. Re-reduction of this solution positive of couple (III), formed the starting species with ca.

50% loss of the Q band intensity; however the spectrum was identical in shape to the initial spectrum and no decomposition products absorbing in the 300-1600 nm region were observed. To our knowledge, no report has previously been made of a phthalocyanine third oxidation product. In view of the similarity of the potential to that of the second ligand oxidation of H_2TNPc, and the fact that the electronic spectrum (Figure 7) is very different from the $Pc(-1)$ species, it is likely that this is also the second ligand oxidation, to give $[Co(III)TNPc(0)]^{3+}$, rather than $[Co(IV)TNPc(-1)]^{3+}$.

Electrochemistry in DMF Solution

Figure 2(b) shows a typical cyclic voltammogram for CoTNPc in DMF, with half-wave potentials and peak separations at 20 mV/s given in Table I. The reduction processes are very similar to those found in DCB solution, having two quasi-reversible one-electron couples separated by ca. 1.15 V; however, marked changes are seen for the oxidation processes. The reversibility of the first oxidation wave (III) is strongly dependent both upon scan rate and the upper positive limit of the voltage sweep. If the voltage sweep is reversed at a potential negative of the second oxidation couple (II), a broad flat irreversible return wave is obtained at slow sweep rates, which increases in magnitude with increasing sweep rate, as shown in Figure 8(a).

Sweeping the potential positive of the second oxidation potential results in an increase in the return wave for a given sweep rate, although at very slow scan rates (2 mV/s) the return wave is still irreversible (Figure 8(b)). The second oxidation exhibits two anodic and two cathodic waves, as shown in Figure 8(b). At high sweep rates

(Figure 8(c)) (100 mV/s), the more positive wave is dominant, with only a shoulder occurring at ca. +0.3 V, and a single return wave. As the sweep rate is decreased, the contribution from the more negative couple increases, so that the return wave splits into two peaks. Before discussing the significance of these data, it is useful to review the spectro-electrochemical data.

Spectro-electrochemistry in DMF

Controlled potential electrolysis in the OTTLE of a solution of CoTNPc in DMF at 200 mV positive of the first oxidation couple (III) results in the spectroscopic changes shown in Figure 9, and the formation of a blue-green solution. This spectrum, characterised by a red-shift, increase in intensity and sharpening of the Q band and a red-shift of the Soret band relative to the starting spectrum, is similar to those observed for the Co(III)Pc species, $[Co(III)(X)_2Pc(-2)]^-$ (X = OH, F, Cl or Br)[47], $[Co(III)(OH)_2TNPc(-2)]^{-34}$, $[Co(III)(CN)_2Pc(-2)]^{-39,40,48}$ and $[Co(III)(CN)_2TNPc]^{1-}$ (this work). Thus, in DMF solution, the first oxidation (III) indeed occurs on the cobalt rather than the phthalocyanine ring.

Polarisation in the OTTLE at potentials positive of the oxidation couple (II) resulted in a fairly rapid loss of the phthalocyanine absorption. However, the spectrum of the oxidised species was obtained using the bulk cell/Guided Wave spectrometer arrangement. The spectrum was very similar to that of the second oxidation in DCB (see Table II), albeit with the bands red-shifted by 50 – 90 nm with respect to DCB solution. Thus couples (III) and (II) in DMF correspond to the

formation of $[Co(III)TNPc(-2)]^+$ and $[Co(III)TNPc(-1)]^{2+}$, respectively.

The binuclear cobalt phthalocyanines gave essentially similar spectro-electrochemistry to CoTNPc. The spectra of the redox products were those expected for complete oxidation or reduction of the two CoTrNPc units at each redox couple, with no evidence for the formation of any mixed valence states. As an example, the spectrum of the second reduction product of O(1)[CoTrNPc]$_2$ is shown also in Figure 6. Of note, the absorption of the ligand reduced species was rather more broad in the binuclear complexes, probably as a consequence of coupling.[34]

Discussion of Electrochemical Behaviour in DMF

The bulk solute in DMF is expected to be the five coordinate DMFCo(II)TNPc(-2) based upon earlier studies which show the prevalence of five coordinate Co(II)Pc species.[53]

Since the axial site is expected to be labile, there will be other species in equilibrium. The most important are likely to be:-

$$DMFCo(II)Pc(-2) \iff (DMF)_2Co(II)TNPc(-2) \iff [(DMF)(ClO_4)Co(II)TNPc(-2)]^-$$

(A)   (B)   (C)
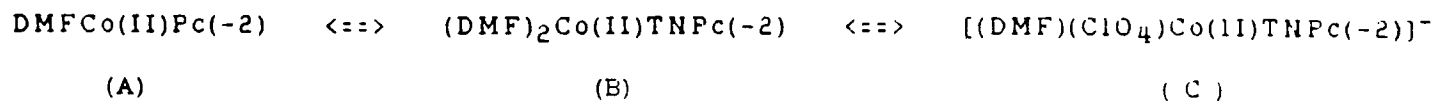
(1)

One may readily predict that species (C) will oxidise at the least positive potential.[18] Thus in Figure 8 the anodic wave (IIa) corresponds to oxidation of species (C), formed very rapidly at the electrode in a CE reaction. Given that the ClO_4^-:Co(II)TNPc ratio is so large, and that there is an axial site vacant on the phthalocyanine, the rate of perchlorate ion incorporation is probably diffusion

controlled.

When the switching potential lies between couples (II) and (III), the cathodic wave corresponding to (IIIa) diminishes in current quite dramatically with slower scan rate, and the ratio i_c/i_a is considerably less than unity (Table III). At higher scan rates, this ratio equals unity. Thus the couple is irreversible at very slow scan rates. These ratios are subject to some uncertainty given the close proximity of the next redox couple, so that calculation of rate constants therefrom would be unreliable. We note that, at a given scan rate, the i_c/i_a ratio increases with increasing perchlorate ion concentration, supporting the view that species (C) is involved as proposed. The product on the electrode after oxidation is the six coordinate $[DMF(ClO_4)Co(III)TNPc(-2)]$. This will participate in an equilibrium (2) in which either the DMF or perchlorato groups are lost to form a five coordinate species which is much more readily reducible to Co(II) than is the six coordinate species and thus has a redox potential positive of couple (III).

$$[DMF(ClO_4)Co(III)Pc(-2)] \rightleftharpoons DMF + [ClO_4Co(III)Pc(-2)]$$
$$\rightleftharpoons ClO_4^- + [DMFCo(III)Pc(-2)]^+$$
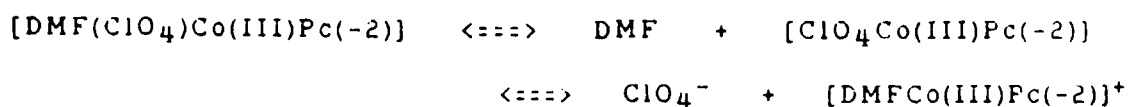
$$(2)$$

Although this five coordinate Co(III) species is likely to be formed in only minute amounts, the equilibrium should be sufficiently facile that during the time of the cathodic sweep positive of couple (III), some of the Co(III) species on the electrode is reduced and therefore does not contribute current to cathodic wave (IIIc). Clearly the slower the sweep, the greater the loss in cathodic current in (IIIc). Previous studies[54] show that although axial substitution of six coordinate Co(III) species is usually very slow indeed, axial sites on Co(III)

macrocycles   are   more   labile.

Beyond (IIIa) the next process is oxidation   to
$[DMF(ClO_4)Co(III)TNPc(-1)]^+$ reasonably   associated   with   the   major
oxidation   peak   (IIa).   Although   in   the   spectro-electrochemical
experiment,   this   species   is   unstable,   it   is   evidently   sufficiently
stable   in   the   much   shorter   time   frame   of   the   cyclic   voltammetry
experiment.   There   are   two   clearly   identifiable   cathodic   peaks   whose
relative   intensity   changes   with   scan   rate   (Figure   8b).   With   increasing
scan   rate   the   more   positive   wave   (IIc)   grows   at   the   expense   of   the   less
positive   wave   (II'c),   and   vice   versa   at   slower   scan   rates.   Moreover
with   increasing   perchlorate   ion   concentration   (0.1   -   0.3M),   the   less
positive   wave   grows   slightly,   at   the   expense   of   the   more   positive   wave.
The   most   positive   reduction   wave,   (IIc),   must   correspond   with   the
reduction   of $[DMF(ClO_4)Co(III)TNPc(-1)]^+$.   Wave   (II'c)   must   involve
additional   perchlorate   ion   and   is   reasonably   associated   with   reduction
of $[(ClO_4)_2Co(III)TNPc(-1)]$ formed   by   a   slow   substitution   of   DMF   by
perchlorate   ion   in $[DMF(ClO_4)Co(III)TNPc(-1)]^+$.

On   the   anodic   component   of   couple   (II),   there   is   a   very   weak   lower
potential   shoulder   which   is   more   evident   at   slow   scan   rates   (Figure
8(b))   and   is   marginally   enhanced   by   increasing   perchlorate   ion
concentration.   This   is   likely   to   be   the   anodic   partner   to   (II'c)   formed
by   very   slow   substitution   of   DMF   by   perchlorate   ion   in
$[DMF(ClO_4)Co(III)TNPc(-2)]$ formed   on   the   electrode   surface.   The   redox
couple   for   the   bis-perchlorato   species   (II')   lies   at   a   (slightly)   lower
potential   than   for   the   mono-perchlorato   species,   as   would   be
anticipated   because   of   the   extra   charge   disposed   onto   the   cobalt   ion.[18]

When   the   switching   potential   is   positive   of   couple   (II),   the
cathodic   return   wave   for   couple   (III)   is   not   diminished   except   at

exceptionally slow scan rates, the i_c/i_a ratio remaining unity. Assuming that the above mechanism for irreversibility is correct, it follows that the species now on the electrode must be different from the previous switching situation and must dissociate a ligand rather more slowly. Indeed at the slow scan rates necessary to observe this phenomenon, the species on the electrode when switched beyond couple (II), will be $[(ClO_4)_2Co(III)TNPc(-2)]^-$ which must then have a slower dissociation rate. This bis-perchlorato species would be expected to have a somewhat less positive reduction potential than the $[DMF(ClO_4)Co(III)TNPc(-2)]$ species, yet this appears experimentally not to be the case. Possibly the difference is too small to be evident.

Previously, Kelly and Kadish[12] had shown that $DMF(Cl)Cr(III)TPP$ and $[(DMF)_2Cr(III)TPP]^+$ both reduce at the same potential, in DMF, and explain this by assuming that a CE reaction occurs, with chloride being replaced by DMF at the electrode in a reaction driven by the applied potential. This is the same argument being used here to infer which cobalt species is active at each couple.

Thus, in summary, the species involved in the region of couples (II) and (III) are (vs Fc^+/Fc):-

$[DMF(ClO_4)Co(III)TNPc(-2)/DMF(ClO_4)Co(II)TNPc(-2)^-]$ $E_{1/2}$ = $-0.02V$

$[DMF(ClO_4)Co(III)TNPc(-1)^+/DMF(ClO_4)Co(III)TNPc(-2)]$ $E_{1/2}$ = $+0.38V$

$[(ClO_4)_2Co(III)TNPc(-1)/(ClO_4)_2Co(III)TNPc(-2)^-]$ $E_{1/2}$ = $+0.30V$
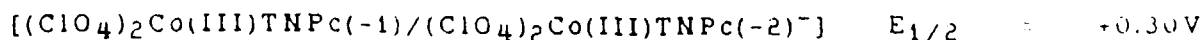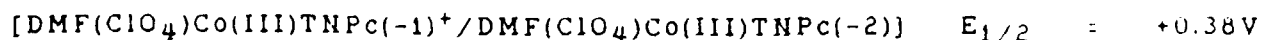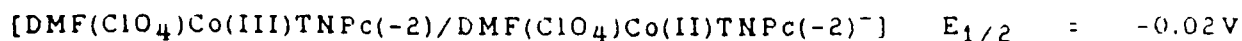
The overall redox behaviour is shown in Scheme I.

Rationalisation   with   the   Literature.

There   are   scattered   reports   of   the   spectra   of   phthalocyanine   anion
and   cation   radical   species   in   the   literature,   as   referenced   above,   but
this   is   the   first   study   where   the   spectra   of   one   species   have   been
followed   through   seven   oxidation   states.   Cation   radical   spectra   have
only   rarely   been   reported   in   the   solution   state.

It   is   tempting   to   try   to   assign   the   spectra   of   the   various
oxidation   species   reported   here   and   compare   the   data   with   those   for
related   materials   in   the   literature.   Indeed   we   have   previously
predicted   the   type   of   spectra   to   be   anticipated   for   metallo-
phthalocyanines   in   various   oxidation   states [46];   however,   in   the   absence
of   supporting   data   such   as   MCD[49],   it   would   be   foolhardy   to   try   and
assign,   in   any   detail,   the   rather   broad   and   overlapping   bands   commonly
observed   for   these   various   species   (e.g.   Figure   7).

Phthalocyanine   cation   radical   (Pc(-1))   spectra   are   now   known   for   a
range   of   metal   ions   including   Co(II),   Co(III),   Ru(II),   Rh(III),
Fe(III),   Cr(III),   Zn(II),   Si(IV), H_2,   Mg   and   Cu(II).[21,22,37,46,
47,49,55,56]   These   all   appear   to   show   medium   intensity   bands   near
700-800nm   and   near   500nm.   The   former   is   assigned   as   a   transition   from   a
lower   lying e_g π level   into   the   hole   in   the   HOMO π level.[46,49,55]
Charge   transfer   spectra   from   metal   d   levels   to   the   hole   in   the   HOMO
level   can   be   anticipated,   but   have   not   been   identified.[49]

The   voltammetry   of H_2TNPc   and   CoTNPc   is   summarised   and   compared
with   that   of H_2TPP[8,9,11,15,16,57-59]   and   CoTPP[3-8,15,16,58]   in   the   form
of   a   redox   potential   state   diagram   in   Figure   10.   Complexation   with
cobalt   (II)   causes   a   negative   shift   in   the   potential   of   the   first
ligand   reduction   by   ca.   500   mV   in   non-coordinating   solvents   for   both

TNPc and TPP (Figure 10), as a result of the insertion of the cobalt d orbitals between the HOMO and LUMO orbitals of the ring. The potential of the first ligand oxidation also shifts negatively, but to a lesser extent, resulting in a net increase in separation between the first oxidation and reduction couples (E[L$^+$/L] – E[L/L$^-$] = 2.1 and 2.9 V for CoTNPc and CoTPP, respectively).[3-5,7,8,58] Notably, the L/L$^-$, Co(II)/Co(I) and Co(III)/II) couples of CoTNPc and CoTPP lie at similar potentials in non-coordinating solvents (Figure 10). For both compounds, the Co(II)/Co(I) couple lies positive of the first ligand reduction, so that the cobalt is reduced first. However, differences are seen in the oxidation processes. For CoTNPc, the separation between the HOMO and LUMO orbitals of the ring is small enough to leave the L$^+$/L couple negative of the Co(III)/Co(II) couple, so that oxidation occurs at the ring first. For CoTPP, however, the larger separation of the HOMO and LUMO orbitals results in the L$^+$/L couple lying positive of the Co(III)/Co(II) couple, even in non- coordinating solvents. The relative positions of the cobalt d orbitals and TNPc HOMO also results in a large increase in separation of the first and second ligand oxidations compared with the metal-free complex, while for porphyrins a small decrease in separation of the couples is seen.[4,5,7,11,15,16]

In DMF, the Co(III)/Co(II) couple of CoTNPc shifts negatively by ca. 600 mV, as a result of the stabilisation of the Co(III) species in the presence of the axially coordinating solvent, while the L$^+$/L couple shifts positively by 300 mV, as a consequence of the presence of the highly polarising central ion (Co(III)).[60] Thus, the first oxidation now occurs at the cobalt atom. Similarly, the Co(III)/Co(II) couple shifts negatively by almost 800 mV for CoTPP on going from DCM to DMF solution.[4] The potential of the Co(II)/Co(I) couple remains

approximately   constant,   as   expected   for   the   four-coordinate   Co(I)   species.

Data   for   the   binuclear   species   are   somewhat   disappointing   given   that   they   differ   little   from   the   mononuclear   analog.   The   binuclear   species   are   significantly,   but   not   dramatically,   more   efficient   for   oxygen   reduction[26],   than   the   mononuclear   control.   More   tightly   coupled   binuclear   phthalocyanines   are   currently   under   investigation.

Acknowledgements

References

1. Current address: Department of Chemistry, Yangzhou Teachers'
    College, Yangzhou, Jiangsu, People's Republic of China.

2. Fajer,J.; Borg,D.C.; Forman,A.; Dolphin,D.; Felton,R.H.,
    J.Am.Chem.Soc., 1970, 92, 3451.

3. Wolberg,A.; Manassen,J., J.Am.Chem.Soc., 1970, 92, 2982.

4. Truxillo,L.A.; Davis,D.G., Anal.Chem., 1975, 47, 2260.

5. Lin,X.Q.; Kadish,K.M., Anal.Chem., 1985, 57, 1498.

6. Kelly,S.; Lancon,D.; Kadish,K.M., Inorg.Chem., 1984, 23, 1451.

7. Walker,F.A.; Beroiz,D.; Kadish,K.M., J.Am.Chem.Soc., 1976,
    98, 3484.

8. Felton,R.H.; Linschitz,L., J.Am.Chem.Soc., 1966, 88, 1113.

9. Peychal-Heiling,G.; Wilson,G.S., Anal.Chem., 1971, 43, 550.

10. Fuhrhop,J.-H.; Kadish,K.M.; Davis,D.G., J.Am.Chem.Soc.,
    1973, 95, 5140.

11. Brown,G.M.; Hopf,F.R.; Ferguson,J.A.; Whitten,D.G., J.Am.Chem.Soc.
    1973, 95, 5939.

12. Kelly,S.L.; Kadish,K.M., Inorg.Chem., 1984, 23, 679.

13. Collman,J.P.; Marrocco,M.; Elliot,C.M.; L'Her,M.,
    J.Electroanal.Chem., 1982, 124, 113.

14. Le Mest,Y.; L'Her,M,; Courtot-Coupez,J.; Collman,J.P.;
    Evitt,E.R.; Bencosme,C.S., J.Electroanal.Chem., 1984, 184, 331.

15. Felton,R.H. In "The Porphyrins"; Dolphin,D.,Ed.; Academic
    Press: New York, 1978; Vol.V, Chapter 3.

16. Davis,D.G. In "The Porphyrins"; Dolphin,D.,Ed.; Academic
    Press: New York, 1978; Vol.V, Chapter 4.

17. Nevin,W.A.; Liu,W.; Melnik,M.; Lever,A.B.P., J.Electroanal.Chem. 1986, $\underline{000}$, 0000.

18. Lever,A.B.P.; Wilshire,J.P., Inorg.Chem., 1978, $\underline{17}$, 1145.

19. Rollmann,L.D.; Iwamoto,R.T., J.Am.Chem.Soc., 1968, $\underline{90}$, 1455.

20. Clack,D.W.; Yandle,J.R., Inorg.Chem., 1972, $\underline{11}$, 1738.

21. Dolphin,D.; James,B.R.; Murray,A.J.; Thornback,J.R., Can.J.Chem. 1980, $\underline{58}$, 1125.

22. Ferraudi,G.; Oishi,S.; Muraldiharan,S., J.Phys.Chem., 1984, $\underline{88}$, 5261.

23. Bottomley,L.A.; Gorce,J.-N.; Goedken,V.L.; Ercolani,C., Inorg.Chem. 1985, $\underline{24}$, 3733.

24. Gavrilov,V.I.; Tomilova,L.G.; Shelepin,I.V.; Luk'yanets, Elektrokhimiya, 1979, $\underline{15}$, 1058.

25. Kobayashi,N.; Shirai,H.; Hojo,N., J.Chem.Soc. Dalton 1984, 2107; Kobayashi,N.; Nishiyama,Y., J.Phys.Chem., 1985 $\underline{89}$, 1167.

26. Hempstead,M.R.; Lever,A.B.P.; Leznoff,C.C.,   to be submitted.

27. Lieber,C.M.; Lewis,N.S., J.am.Chem.Soc., 1984, $\underline{106}$. 5033.

28. Hirai,T.;   Yamaki,J.,   J.Electrochem.Soc.,   1985, $\underline{132}$,   2125; Simic-Glavaski,B.; Zecevic,S.; Yeager,E., J.Electroanal Chem., 1983, $\underline{150}$, 469; ibid J.Phys.Chem., 1983, $\underline{87}$, 4555.

29. Collins,G.C.S.; Schiffrin,D.J., J.Electroanal.Chem., 1982, $\underline{139}$, 335; M'Sadak,M.; Roncali,J.; Garnier,F., J.Electroanal.Chem., 1985, $\underline{189}$, 99.

30. Nicholson,M.M.; Pizzarello,F.A., J.Electroanal.Chem.. 1981, $\underline{128}$, 1289, 1740.

31. Leznoff,C.C.; Greenberg,S.; Marcuccio,S.M.; Minor,P.C.; Seymour,P; Lever,A.B.P., Inorg. Chim. Acta, 1984, $\underline{89}$, L35;

Leznoff,C.C.;   Marcuccio,S.M.;   Greenberg,S.;   Lever,A.B.P.;
Tomer,K.B., Can. J. Chem., 1985, 63, 623.

32.   Marcuccio,S.M.;   Svirskaya,P.I.;   Greenberg,S.;   Lever,A.B.P.;
Leznoff,C.C., Can. J. Chem., 1985, 63, 3057.

33.   Greenberg,S.;   Marcuccio,S.M.;   Leznoff,C.C.,   Synthesis,   1986,   406

34.   Liu.W.;   Nevin,W.A.;   Hempstead,M.R.;   Melnik,M.;   Lever,A.B.P.;
Leznoff,C.C.,   submitted   to   Inorg.Chem.

35.   Dodsworth,E.S.;   Lever,A.B.P.;   Seymour,P.;   Leznoff,C.C.,
J.Phys.Chem.,1985,   89,   5698.

36.   The   symbol   Pc(-2)   refers   to   the   di-negatively   charged
phthalocyanine   unit   in   its   standard   oxidation   state.   The
first   ring-oxidised   species   is   the   radical   Pc(-1)   and   the
first   ring-reduced   species   is   the   radical   Pc(-3).[37]

37.   Myers,J.F.;   Rayner-Canham,G.W.;   Lever,A.B.P.,   Inorg.Chem.,   1975
14,   461.

38.   Metz,J.;   Hanack,M.,   J.Am.Chem.Soc.,   1983,   105,   828.

39.   Day,P.;   Hill,H.A.O.;   Price,M.G.,   J.Chem.Soc.,   A,   1968,   90.

40.   Stillman,M.J.;   Thompson,A.J.,   J.Chem.Soc.,   Faraday   Trans.   II,
1974,   70,   790.

41.   Gagne,R.R.;   Koval,C.A.;   Lisensky,D.C.,   Inorg.Chem.,   1980,
19,   2854;   Gritzner,G.;   Kuta,J.,   Electrochim.   Acta,   1984,   29,   869.

42.   Nevin,W.A.;   Lever,A.B.P.,   to   be   submitted.

43.   Le   Moigne,J.;   Even,R.,   J.   Chem.   Phys.,   1985,   82,   6472.

44.   Taube,R.,   Z.   Chem.,   1966,   6,   8.

45.   Lever,A.B.P.;   Licoccia,S.;   Magnell,K.;   Minor,P.C.;
Ramaswamy,B.S.,   A.C.S.   Symposium   Ser.,   1982,   201,   237.

46.   Minor,P.C.;   Gouterman,M.;   Lever,A.B.P.,   Inorg.Chem.,   1985,
24,   1894.

47.   Homburg,H.;   Kaltz,W.,   Z.   Naturforsch.,   1984,   39b,   1490.

48.   Kalz,W.;   Homborg,H.;   Kuppers,H.;   Kennedy,B.J.;   Murray,K.S.,

Z.   Naturforsch.,   1984,   39b,   1478.

49.   Nyokong,T.;   Gasyna,Z.;   Stillman,   M.J.,   Inorg.   Chim.   Acta,   1986

112,   11.

50.   Fuhrhop,J.-H.;   Wasser,P.;   Riesner,D.;   Mauzerall,D.,   J.Am.Chem.Soc.,

1972,   94,   7996.

51.   Dolphin,D.;   Felton,R.H.,   Acc.   Chem.   Res.,   1974,   7,   26.

52.   Fuhrhop,J.-H.,   Struct.   Bonding,   Berlin,   1974,   18,   1.

53.   Cariati,   F.;   Gallizzioli,   D.;   Morazzoni,   F,   Busetto,   C,   J.Chem.Soc.

Dalton,   1975,   556-61;   Cariati,   F.;   Morazzoni,   F.;   Busetto,   C,

J.Chem.Soc.   Dalton,   1976,   496-500.

54.   Fleischer,   E.   B.;   Jacobs,   S.;   Mestichelli,   L.,   J.Am.Chem.Soc.,

1968,   90,   2527.

55.   Nyokong,T.;   Gasyna,Z.;   Stillman,M.J.,   private   communication.

56.   Homborg,H.,   Z.anorg.allgem.Chem.,   1983,   507,   35.

57.   Kadish,K.M.;   Thompson,L.K.;   Beroiz,D.;   Bottomley,L.A.,   ACS   Symposium

Ser.   1977,   38,   51.

58.   Wolberg,A.,   Isr.   J.   Chem.,   1974,   12,   1031.

59.   Lexa,D.;   Riex,M.,   J.   Chim.   Phys.,   1974,   71,   511.

60.   Lever,A.B.P.;   Minor,P.C.,   Inorg.Chem.,   1981,   20,   4015.

Legends

Figure 1. Binuclear phthalocyanine compounds.

Figure 2. Cyclic voltammetry of CoTNPc (a) in DCB solution (Ft working electrode) and (b) in DMF solution (Ft wire working electro Scan rate = 50 mV/s, [CoTNPc] = 1 x 10^{-4}M, [TBAP] = 0.3M.

Figure 3. Differential pulse polarograms of (a) CoTNPc and O(1)[CoTrNPc]$_2$ in DCB solution (0.3M TBAP). Scan rate = 2 mV [CoTNPc] = 1 x 10^{-4}M, [O(1)[CoTrNPc]$_2$] = ca. 5 x 10^{-5}M.

Figure 4. Electronic absorption spectra of Co(II)TNPc(-2) (——), EtMeO(5)[Co(II)TrNPc(-2)]$_2$ (----), and C(2)[Co(II)TrNFc(-2)]$_2$ (....) in {[Pc] x pathlength = constant}

Figure 5. Development of the electronic absorption spectra with time du the reduction of Co(II)TNPc(-2) at -1.1V vs Fc$^+$/Fc in DCB (0.3M TBA [CoTNPc] = 1.2 x 10^{-4}M.

Figure 6. Electronic absorption spectra of electrochemically genera [Co(I)THPc(-3)]$^{2-}$ (——) and O(1)[Co(I)TrNFc(-3)]$_2$$^{4-}$ (----) in DCB (C TBAP). [CoTNPc] = 9 x 10^{-5}M, [O(1)[CoTrNPc]$_2$] - 4 x 10^{-5}M.

Figure 7. Electronic spectra of electrochemically generat [Co(II)TNPc(-1)]$^+$ (----), [Co(III)TNPc(-1)]$^{2+}$ (.....) an [Co(III)THPc(0)]$^{3+}$ (——) species in DCB (0.3M TBAP). [CoTNPc] = 5 x 10^-

Figure 8. Cyclic voltammetry of CoTNPc in DMF (0.3M TBAP) at various scan rates and switching potentials. (a) The Co(III)/Co(II) couple at 2,5,10 and 20 mV/s, (b) Pc(-1)/Pc(-2) and Co(III)/Co(II) couples at 2,5,10 and 20 mV/s, and (c) Pc(-1)/Pc(-2) and Co(III)/Co(II) couples at 20,50 and 100 mV/s. [CoTNPc] = 1 x 10^{-4}M.

Figure 9. Development of the electronic absorption spectra with time dur the oxidation of Co(II)TNPc(-2) at +0.2V vs Fc$^+$/Fc in DMF (0.3M TBAP). [CoTNPc] = 2.3 x 10^{-4}M.

Figure 10. Summary of the electrochemistry of H$_2$TNPc and Co(II)TNPc(-2) comparison with H$_2$TPP and CoTPP.

Table I. Electrochemical Data for Mononuclear and Binuclear Neopentoxy Phthalocyanines.

| | $E_{1/2}$ V. $(\Delta E_p, mV)^a$ | | | | |
| | Oxidation | | | Reduction | |
Compound	I	II[c]	III	IV	V
H_2TNPc	+0.77		+0.28	-1.35	-1.70(70)
CoTNPc	+0.87(102)	+0.59(90)	+0.03(89)	-0.91(70)	-2.07(80)
CoTNPc[b]		+0.38[d]	-0.02	-0.85(85)	-1.99(85)
EtMeO(5)[CoTrNPc]$_2$	+0.87	e	+0.05(165)	-0.93	-2.07(85)
CaT(4)[CoTrNPc]$_2$	+0.89	e	+0.03	-0.93	-2.07(95)
C(2)[CoTrNPc]$_2$[f]	+0.87	+0.33	+0.03	-0.94	-2.07
O(1)[CoTrNPc]$_2$[f]	+0.91	+0.51	+0.04	-0.93	-2.07

[a]DCB solution except for [b]DMF solution. Potentials are reported with respect to the ferrocenium/ferrocene couple. $E_{1/2}$ measured by cyclic voltammetry at 100, 50 and 20 mV/s [$E_{1/2}$ = $(E_{pa} + E_{pc})/2$] or differential pulse polarography at 2 mV/s gave essentially identical potentials. Values of ΔE_p (= $E_{pa} - E_{pc}$) are given for a potential sweep rate of 20 mV/s. See text for assignment of couples I-V. [c]The potential of this couple in DCB is very sensitive to traces of coordinating anions. [d]Weak shoulder at 0.30V, see text, labelled couple (II'). [e]Not resolved. [f]Additional weak waves are seen at -1.36 and -1.7V as a consequence of aggregation.

Table 11 Electronic Absorption Maxima of CoTNPc Species

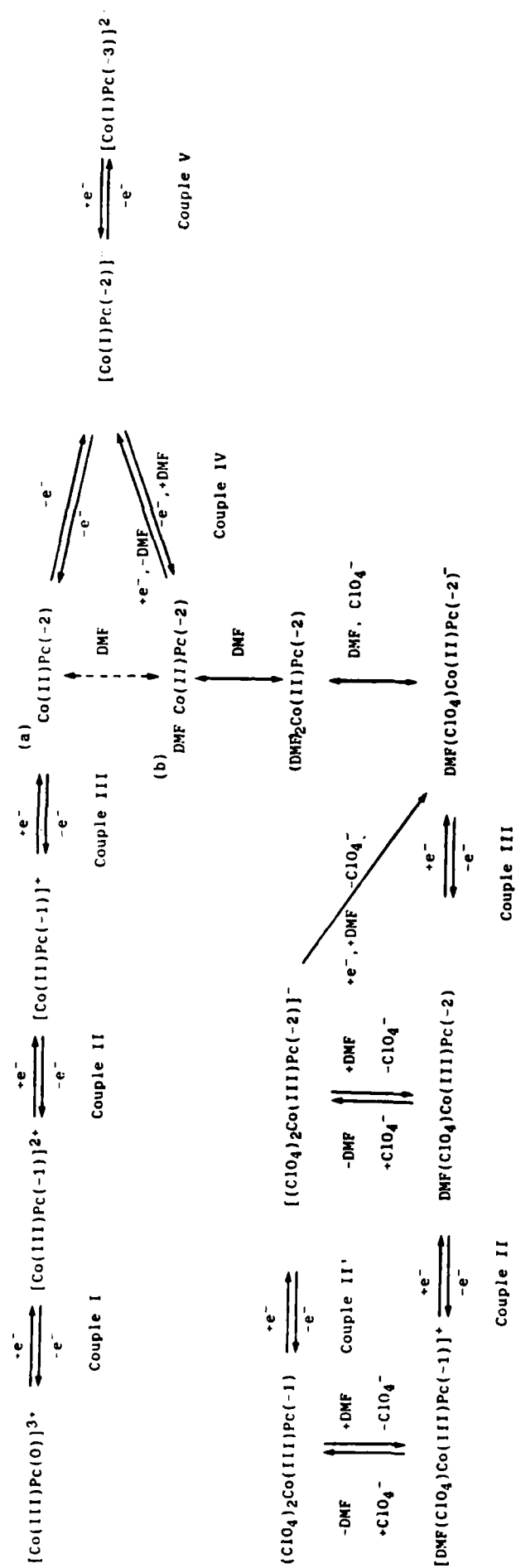| Species[a]	λ_{max}, nm($\epsilon \times 10^{-4} M^{-1} cm^{-1}$)										
[Co(I)TNPc(-3)]²⁻	315 sh	345 sh		480 (3.53)	520 sh	560 sh		640 (1.13)		703 (2.35)	955 (0.32)
[Co(I)TNPc(-2)]⁻	313 (5.79)	350 sh	435 sh	471 (3.33)	520 sh	560 vw	600 sh	643 (1.84)	675 sh	708 (1.50)	
[Co(II)TNPc(-2)]	330 (4.07)	380 (1.38)						612 (2.57)	645 sh	678 (7.21)	
[Co(II)TNPc(-1)]⁻	320 sh	360 sh	405 sh	495 (1.40)		590 sh				606 (1.76)	
[Co(II)TNPc(-1)]²⁻	320 sh	380 (2.36)	400 (2.40)	520 (1.66)			620 (1.64)br			742 (1.15)	
[Co(III)TNPc(0)]³⁻	330 sh	430 br.sh					580 sh				
[Co(II)TNPc(-2)][b]	326 (8.51)	380 sh					620 br				
[Co(III)TNPc(-2)]⁻[b]	340 sh	355 (6.31)						606 (3.89)		668 (10.96)	
[Co(III)TNPc(-1)]²⁻[b]								610 (3.72)		676 (14.79)	
[Co(III)TNPc(-1)]²⁻[b]			405 s	600 m				680 s		795 m	
[Co(III)(CN)₂TNPc(-2)]⁻[c]	355 sh	370 m	440 sh					610 w	645 sh	678 s	

[a] In DCB solution with 0.3 M TBAP except for [b]DMF solution with 0.3 M TBAP and [c] CH₃CN solution. [CoTNPc] = 2×10⁻⁴ M. Note that at these concentrations of phthalocyanine and electrolyte substantial aggregation of the Co(II)TNPc(-2) species occurs. Values of λ_{max}($\epsilon \times 10^{-4} M^{-1} cm^{-1}$) for < 10⁻⁵ M Co(II)TNPc(-2) in pure DCB are 330 (6.54), 382 (2.49), 612 (3.45), 645 sh and 678 (13.5), nm.

br = broad, sh = shoulder, vw = very weak, m = medium, s = strong

Table III Cathodic — Anodic Peak Ratios for CoTNPc Redox Couple III in DMF Solution at Various Scan Rates.[a]

Scan Rate	[TBAP]	i_c/i_a	[TBAP]	i_c/i_a
10 mV/s			0.3 M	0.78
20 mV/s	0.1 M	0.76	- 0.3	0.81
50	0.1	0.77	- 0.3	0.83
100	0.1	0.82	- 0.3	0.86
200	0.1	0.87		
500	0.1	1.00		

[a] [CoTNPc] = 1×10^{-4}M. Positive switching potential lies between couples II and III.

$[Co(III)Pc(0)]^{3+} \xrightarrow[-e^-]{+e^-} [Co(III)Pc(-1)]^{2+} \xrightarrow[-e^-]{+e^-} [Co(II)Pc(-1)]^+$

Couple I   Couple II

(a)

$[Co(II)Pc(-1)]^+ \xrightarrow[-e^-]{+e^-} Co(II)Pc(-2)$

Couple III

$Co(II)Pc(-2) \xrightarrow{\;-e^-\;} [Co(I)Pc(-2)]^-$

$Co(II)Pc(-2) \xrightarrow{DMF}$ (b) DMF Co(II)Pc(-2)

$DMF\,Co(II)Pc(-2) \xrightarrow[+e^-,-DMF]{-e^-,+DMF} [Co(I)Pc(-2)]^-$

Couple IV

$[Co(I)Pc(-2)]^- \xrightarrow[-e^-]{+e^-} [Co(I)Pc(-3)]^{2-}$

Couple V

DMF Co(II)Pc(-2) $\xrightarrow{DMF}$ (DMF)$_2$Co(II)Pc(-2) $\xrightarrow{DMF,\ ClO_4^-}$ DMF(ClO$_4$)Co(II)Pc(-2)$^-$

$(ClO_4)_2Co(III)Pc(-1) \xrightarrow[-e^-]{+e^-} [(ClO_4)_2Co(III)Pc(-2)]^-$

Couple II'

$[(ClO_4)_2Co(III)Pc(-2)]^- \xrightarrow[+ClO_4^-,\ -DMF]{-ClO_4^-,\ +DMF} DMF(ClO_4)Co(II)Pc(-2)^-$

$[(ClO_4)_2Co(III)Pc(-2)]^- \xrightarrow[+ClO_4^-]{-DMF,\ +DMF,\ -ClO_4^-} DMF(ClO_4)Co(III)Pc(-2)$

$(ClO_4)_2Co(III)Pc(-1) \xrightarrow[+ClO_4^-]{+DMF,\ -DMF} [DMF(ClO_4)Co(III)Pc(-1)]^+$

Couple III

$DMF(ClO_4)Co(III)Pc(-2) \xrightarrow[-e^-]{+e^-} DMF(ClO_4)Co(II)Pc(-2)^-$

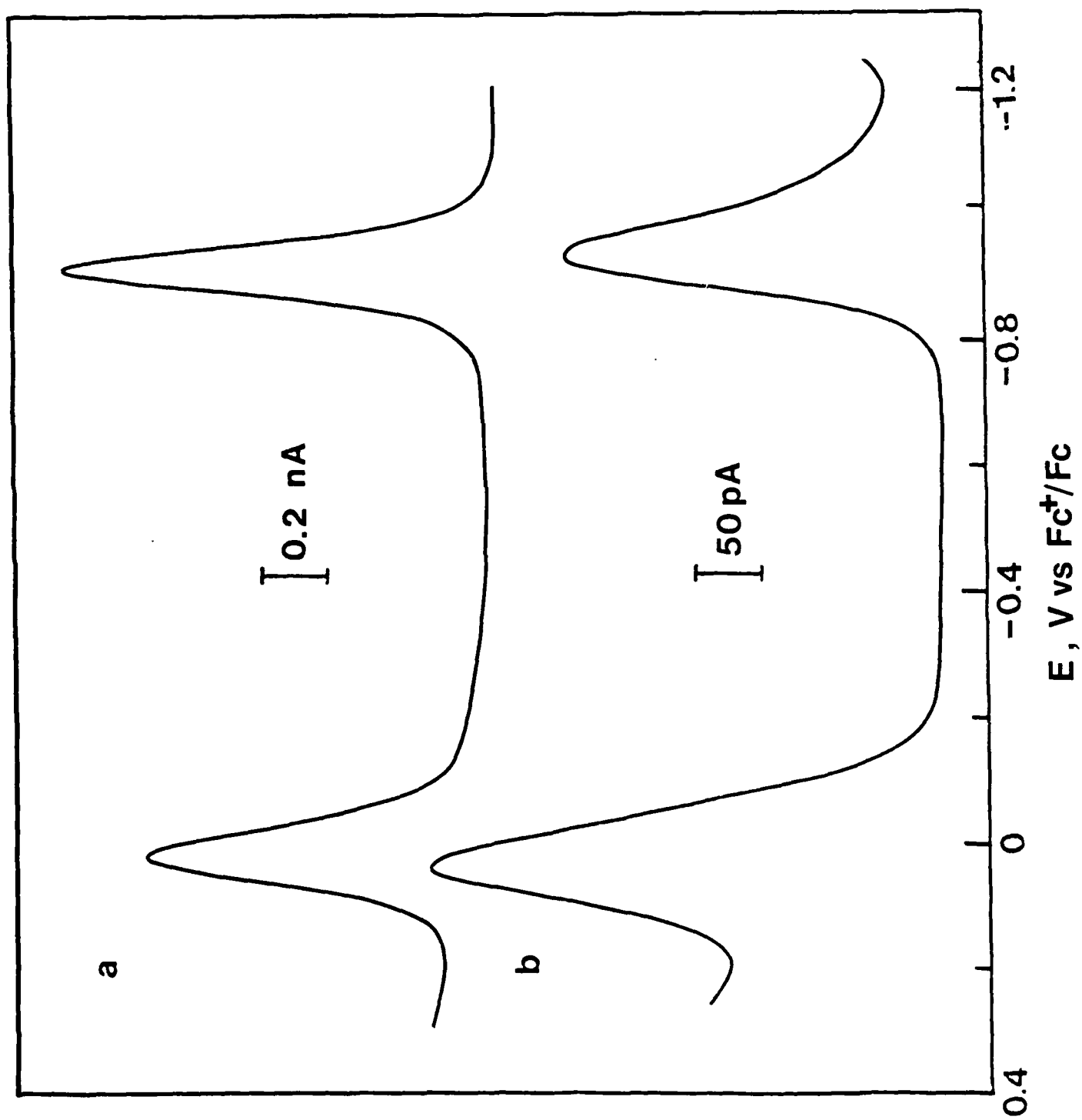$[DMF(ClO_4)Co(III)Pc(-1)]^+ \xrightarrow[-e^-]{+e^-} DMF(ClO_4)Co(III)Pc(-2)$

Couple II

Scheme 1.   Redox equilibria of CoTNPc: (a) in DCB solution.   (b) in DMF solution (Pc=TNPc).

$$R = CH_2C(CH_3)_3 \quad , \quad M = Co$$
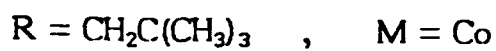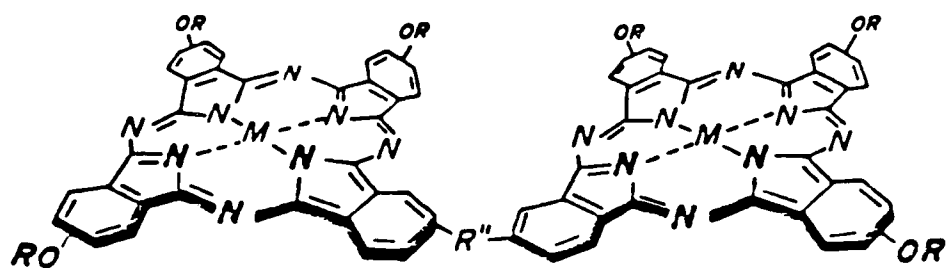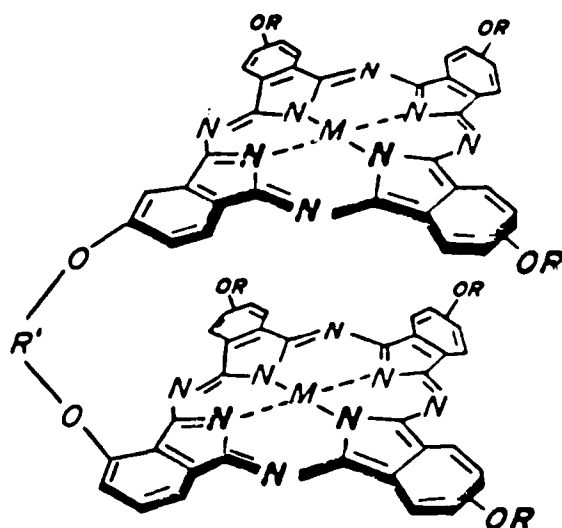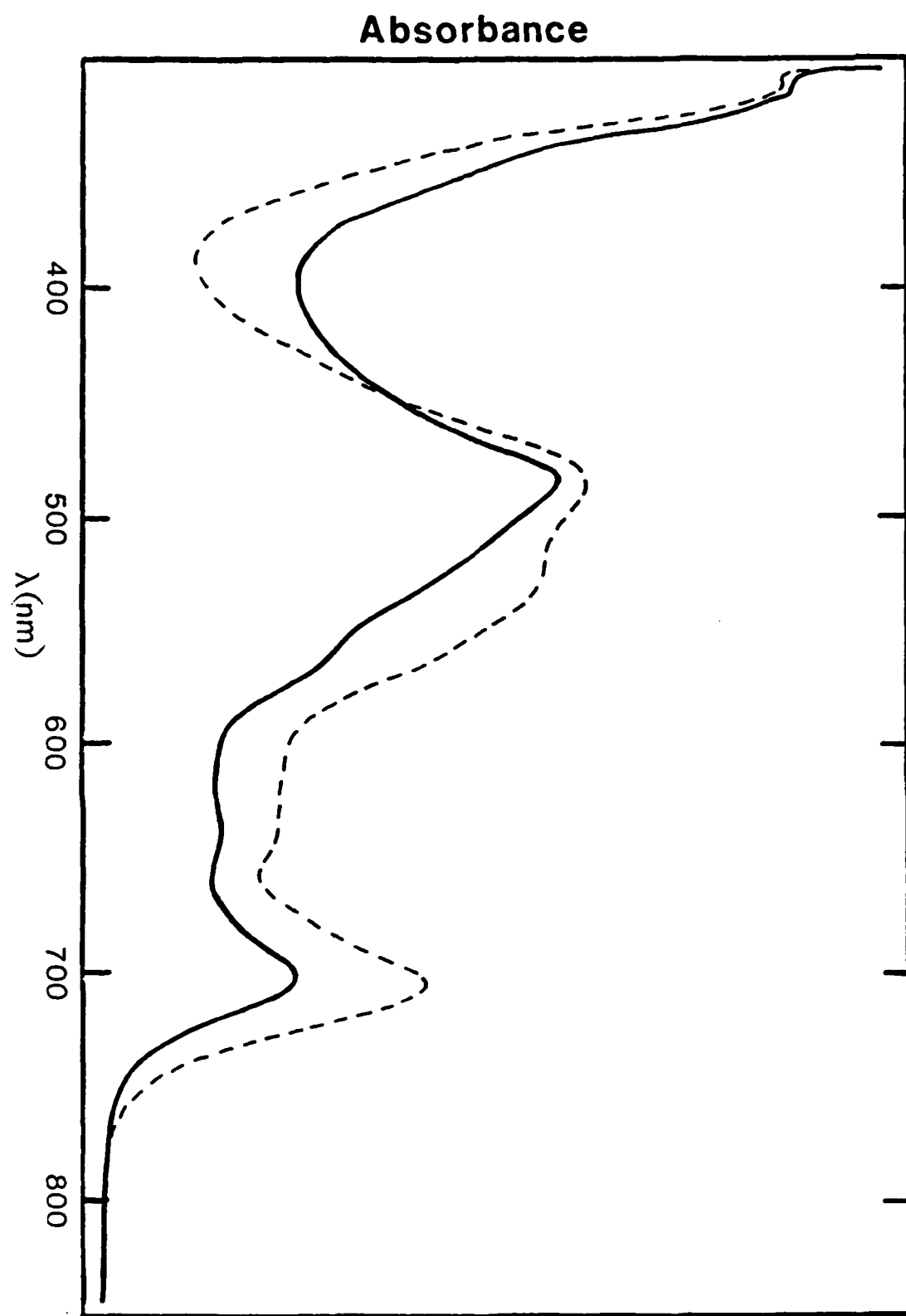
A

EtMeO(5)[CoTrNPc]$_2$, $R' = CH_2C(CH_3CH_2)(CH_3)CH_2$

Cat(4)[CoTrNPc]$_2$, $R' = $ o-phenylene

B

C(2)[CoTrNPc]$_2$, $R'' = CH_2CH_2$

O(1)[CoTrNPc]$_2$, $R'' = O$

a

$\rceil$ 5 nA

b

$\rceil$ 0.5 μA

-1.0   0   1.0   2.0

E, V vs Fc⁺/Fc

0.2 nA

50 pA

a

b

E, V vs Fc⁺/Fc

Absorbance

Wavelength/nm

Absorbance

λ (nm)

a

IIIc

IIIa

0.1 μA

0.2 0 0.2

b

IIIc

IIc

IIć

IIá

IIIa

IIa

0.2 μA

c

IIc

IIIc

IIIa

IIa

0.5 μA

0.6 0.4 0.2 0 0.2

E, V vs Fc⁺/Fc

E, V vs SCE

Figure: Redox potential diagram (E, V vs SCE) comparing H₂TPP/DCM, CoTPP/DCM, H₂TNPc/DCB, CoTNPc/DCB, and CoTNPc/DMF. Ligand redox couples (L^{2+}/L^+, L^+/L, L/L^-, L^-/L^{2-}) and metal couples ($Co^{III/II}$, $Co^{II/I}$) are shown on an energy scale from +1.0 to -2.0 V.

END

12-86

DTIC